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COLLISION WITH SODIUM ATOMS IN ONE
OF THE TWO 3^2P STATES

R. Seiwert

Translation of "Stoesse mit Natrium-Atomen in einem der
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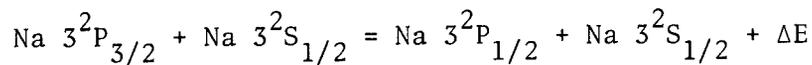
I. INTRODUCTION

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If one of the two D-lines is radiated into a sodium vapor of sufficiently high density, both doublet components will appear in the fluorescent light. This observation was made as far back as 1914 by R. W. Wood [1]. Later, together with F. L. Mohler [2] he studied the effect in more detail, but obtained only semi-quantitative results. W. Lochte-Holtgreven [3], in addition to his measurements of the intensity ratio of the D-lines with admixture of foreign gases, also conducted an experiment with pure sodium vapor in 1928. The results he obtained contradict the results of Wood and Mohler. While the latter found an intensity ratio $\eta_1 = I_{D1}/I_{D2} \approx 0.2$ only at a density¹ of $2.3 \cdot 10^{14}$ atoms/cm³ with irradiation of the D_2 -line, Lochte-Holtgreven observed it at a density of only $4 \cdot 10^{13}$ atoms/cm³.

Collision processes must be viewed as the cause of the appearance of the non-irradiated doublet components in the fluorescent light, said processes being describable by the following reaction equation:

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Here, ΔE is the energy differential between the two 3^2P levels; it amounts to $2.13 \cdot 10^{-3}$ eV.

The goal of our studies was to clarify the discrepancy between the measurement results of Wood and Mohler on the one hand and Lochte-Holtgreven on the

*Numbers in margin indicate foreign text pagination.

¹The words "density" and "vapor density" will be used in this paper to mean "particle density" (number of atoms/cm³).

other and find the cross-sections for the collisions at which a transition² takes place between the resonance levels. Hence, the intensity ratio η of the D-lines must be determined in fluorescent light, with one of the two doublet components being radiated into the sodium vapor; its temperature was varied over a relatively small interval within which these measurements are possible. For completeness² sake, similar studies were performed on a sodium vapor-air mixture and a sodium-potassium vapor mixture.

2. DEPENDENCE OF IMPACT CROSS-SECTION ON RELATIVE VELOCITY OF COLLIDING PARTNERS

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Before discussing the experiments, a brief discussion of the velocity dependence of the impact cross-sections should be represented so that the correspondence between the expectations on the basis of the theoretical calculations and the measurement results can be checked. The impact processes in which a transition takes place between the two resonance levels can be subjected to the application of the principle of the detailed equilibrium, if it is assumed that thermodynamic equilibrium prevails in the alkali vapor, and that the density of the atoms in the excited states corresponds to the temperature of the vapor. In the fluorescent studies this apparently does not apply. The equation, which can be derived on the basis of the principle for the ratio of the cross-sections of the processes occurring in both directions, is not valid for the equilibrium case, however, for each individual collision process (at vapor densities that are not too high) is not influenced by the adjacent atoms. (The ratio of the two impact cross-sections ($q_{12} = q(2P_{1/2} \rightarrow 2P_{3/2})$ and $q_{21} = q(2P_{3/2} \rightarrow 2P_{1/2})$) as a function of the kinetic energy W of the relative moment of the impact partners can be derived by analogy with the studies of O. Klein and S. Rosseland [4] concerning collisions between atoms and free electrons; we will have

$$q_{12}(W - \Delta E) = \frac{g_2}{g_1} \frac{W}{W - \Delta E} q_{21}(W). \quad (2.1)$$

²Here, the possibility has been taken into account that one sodium atom which was initially in the excited state makes the transition to the ground state, but the other sodium atom enters the other excited state, and hence there is a transmission of excitation energy between the collision partners. In the above-mentioned collisions between sodium atoms in one of the two resonance levels with foreign gas atoms (Ar and Ka) only transitions in the strict sense of the word occur, in which a given sodium atom moves from one 3²P state to another.

2 *of the... of the...
A return shall be...*

where g_2 and g_1 are the statistical weights of the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ states and ΔE is the energy differential between the two levels. This equation is also valid for collisions between one alkali atom and one foreign gas atom or molecule in which transitions take place between the two resonance levels. Due to the slight energy differential ΔE ($2.13 \cdot 10^{-3}$ eV in the case of sodium), it is impossible for a conversion of excitation energy into oscillation or rotational energy of the molecule to take place.

On the basis of the energy balance of the collision process, it is evident that q_{12} can only be larger than zero if $W \geq \Delta E$. Further statements regarding the dependence of the cross-sections upon the relative velocity v_r of the collision partners can be made on the basis of "semiclassical" considerations as was shown by H. S. W. Massey and E. H. S. Burhop [5]. If v_r is small, sufficient time will be available for the electron movement within the atom for adjustment to the disturbance to take place, and there is no transition. If the linear extent of the region in which strong interaction forces occur is represented by a , the impact duration is a/v_r . During this time, the system of the two impact partners fluctuates between the initial state and the second state in which the excitation energy differs from that in the initial state by an amount ΔE , with a frequency of the order of $\Delta E/h$. The number of fluctuations during the impact duration is large, and the conditions are nearly adiabatic. Hence, the possibility is not too small that the system will enter another state following the collision:

$$\Delta E \cdot a / h v_r \lesssim 1 \quad (2.2)$$

From this it follows that the frequency of the transitions as a result of collisions increases with decreasing difference of the excitation energy in the two states and with increasing relative velocity of the impact process. At very high values of v_r the adiabatically opposite boundary case occurs which was mentioned by M. Born and J. Franck [6]. The atoms then fly quickly past one another so that at very short impact duration a transition of the system to the other state cannot occur.

Usually a is on the order of magnitude of atomic dimensions; however, it has much higher value if a dipole-dipole-interaction occurs. This is the case

in the instance of energy transmission between levels at which optically permissible transitions are possible at the ground level. The interaction energy is then

$$U(R) \approx \frac{\mu \cdot \mu'}{R^3} \quad (2.2)$$

Here, μ and μ' represent the dipole moments assigned to the transitions and R is the interval of the "radiation dipoles." The size of the area of pronounced interaction can be estimated by assuming that the absolute quantity of interaction energy at the boundary is equal to the energy differential ΔE . Then one obtains a maximally expected impact cross-section

$$q_{\max} \approx \pi \cdot (a/2)^2 \approx \pi \cdot \left(\frac{\mu \cdot \mu'}{\Delta E} \right)^{1/3}; \quad (2.3)$$

for not all impacts in which the collision partners approach to a distance which is equal to or less than $a/2$ lead to an energy transmission because the probability of the latter is dependent in the manner described above upon the relative velocity of the atoms involved in the process. A stricter treatment of the problem [7, 8] leads essentially to the same results. For the impact processes to be investigated between sodium atoms in this paper, $a/2$ has a value of approximately $3 \cdot 10^{-7}$ cm and for q_{\max} approximately $3 \cdot 10^{-13}$ cm². Since at $T = 550^\circ \text{K}$ the average relative velocity v_r is equal to $1 \cdot 10^5$ cm/sec⁻¹, for this temperature one obtains $\Delta E \cdot a/k v_r \approx 3$. We can therefore expect that transitions between the two 3^2P states occur as a result of collisions, but that the corresponding impact cross-sections are located considerably below the estimated maxima.

These "semiclassical" considerations have already provided the characteristic shape of the velocity dependence of the impact cross-section: for very small relative velocities these have a zero value and after passing through the maximum they again tend toward zero with increasing v_r . Equation (2.1) also expresses the ratio of the cross-sections $q_{12}(W + \Delta E)/q_{21}(W)$ for each value of the kinetic energy of the relative motion. In Figure 1, $q_{21}(W)$ is admittedly arbitrary, but the results of the previous considerations are given accordingly and $q_{12}(W)$ is given by equation (2.1).

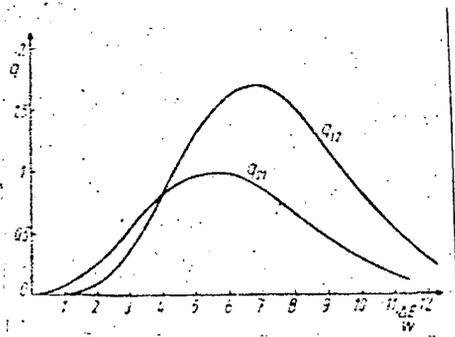


Figure 1. $q = q(W)$. $q_{21}(W)$ is Given and $q_{12}(W)$ is Calculated According to Equation (2.1) with $g_2/g_1 = 2$.

For a specific temperature T of the alkali vapor of the alkali vapor-foreign gas mixture, the impact cross-sections $Q(T)$ and impact number $Z(T)$ can be calculated with the aid of the following equations:

$$Q(T) = \int_0^{\infty} q(W) f_T(W) dW \quad (2.4)$$

and

$$Z(T) = N \left| \frac{2}{M_0} \int_0^{\infty} q(W) \sqrt{W} f_T(W) dW \right| \quad (2.5)$$

Here, the probability that the kinetic energy of the relative motion of the

impact partners is between W and $W + dW$ is

$$f_T(W) dW = \frac{2\sqrt{W}}{\sqrt{\pi} (kT)^{3/2}} \exp\left(-\frac{W}{kT}\right) dW. \quad (2.6)$$

(M is the reduced mass of the impact partners, k is the Boltzmann's constant, N is the density of the atoms in the ground state \approx vapor density).

On the whole, $Q(T)$ and $Z(T)$ have a similar pattern, with increasing T such as $q(W)$ with increasing W , so that $\epsilon(T) = Q_{12}(T)/Q_{21}(T)$ and $\zeta(T) = Z_{12}(T)/Z_{21}(T)$ as $\epsilon'(W) = q_{21}(W)/q_{12}(W)$. It follows from equations (2.4) to (2.6) that by way of approximation we can have the following relationships between the impact cross-sections and the collision numbers

$$Q(T) = \frac{Z(T)}{N \cdot v_r} \quad \text{with} \quad v_r = \sqrt{\frac{8kT}{\pi M}}. \quad (2.7)$$

3. PERFORMANCE OF MEASUREMENTS

3.1. Diagram of Experimental Arrangements

One can see the arrangement of the experiment from Figure 2; the details are shown in Figure 3.

The statement of the problem indicates that a beam in which a D-line was contained passed through the resonance chamber. The latter was located in a furnace that made it possible to regulate both the temperature and the density of the sodium vapor. The fluorescent light was studied at right angles to the exciting beam with the aid of a spectrograph. Three totally reflecting prisms were

arranged in such fashion that a horizontal layer of the fluorescent sodium vapor was imaged on the vertical slit of the spectrograph. This made it possible to determine the intensity ratio of the two D-lines as a function of the distance y of the volume element from the front wall of the cell, from which the fluorescent radiation came.

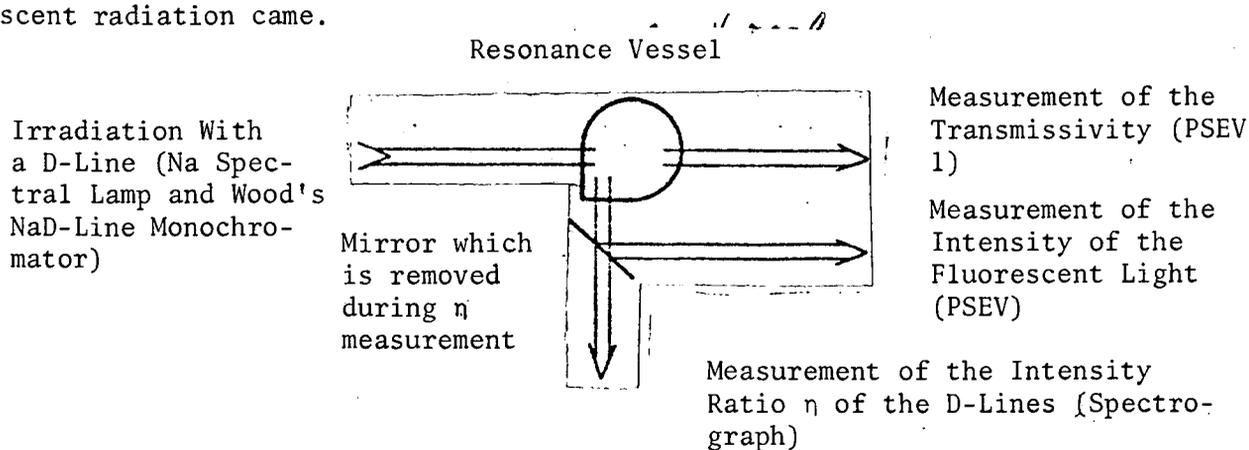


Figure 2. Diagram of Experimental System.

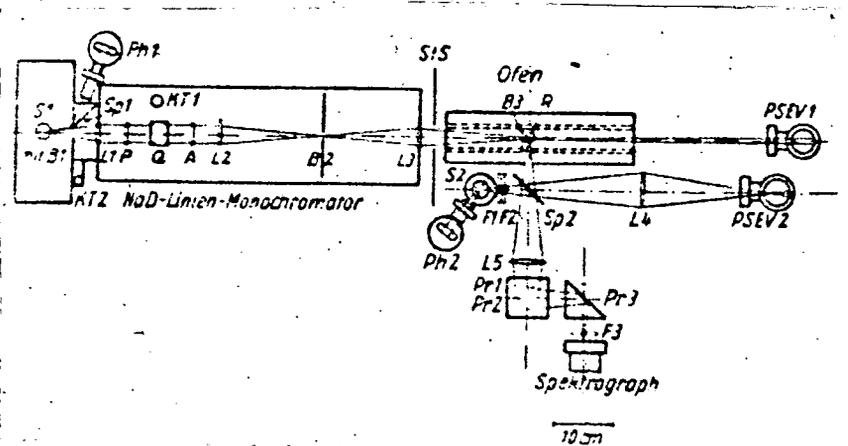


Figure 3. Experimental System. A, analyzer; B1, B2, B3 diaphragms; F1, F2, F3, filters; KT1, KT2, contact thermometers; L1, L2, L3, L4, L5, collimating lenses; P, polarizer; Ph1, Ph2, photocells; Pr1, Pr2, Pr3, totally reflecting prisms; PSEV1, PSEV2, photocathode secondary electron multipliers; Q, quartz plate; R, resonant container, S1, S2, sodium spectral lamps; Sp1, Sp2, mirrors; StS, radiation shield.

By means of a mirror, the fluorescent light could be directed onto the photocathode of a secondary electron multiplier³. Then the intensity of

³"Photocathode secondary electron multiplier" will be abbreviated "PSEV" from now on.

the fluorescent radiation which was not decomposed spectrally could be determined within certain solid angles. These measurements served to monitor the course of the experiment, and also provided important information concerning the processes within the resonance vessel.

A small portion of the light which was transmitted by the sodium vapor in the cuvette fell on the photocathode of a second PSEV. The purpose of these transmissivity measurements was (first of all) to monitor continuously the constancy of the vapor density in the resonance vessel. Small temperature variations result in a large change in the transmitted light flux, since the vapor pressure is approximately proportional to $\exp(-A/kT)$. Thus, the determinations of the transmitted radiation provide a valuable supplement to the measurements with the aid of the thermal elements. Moreover, it is possible to determine transmissivity of the sodium vapor layer from them as a function of temperature; this is discussed in greater detail in Section 35.

32. The Separation of the D-Lines

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The light source was a sodium spectral lamp; the separation of the two resonance lines was performed with the aid of a Wood NaD-line monochromator [12].

Inasmuch as the length of the light path in the quartz plate can be regulated so that the required path difference between the ordinary and extraordinary rays is produced, the quartz plate is rotated around its optical axis. According to the studies of E. Gaviola and P. Pringsheim [13], this has necessarily led to a certain lack of purity in the light transmitted by the monochromator. By mounting a diaphragm directly in front of the discharge vessel of the spectral lamp and using a collimating lens whose focal length is not too short, it is possible to achieve a good degree of parallelism of the light; with the aid of two more diaphragms, it is possible to separate precisely those parts of the light beam which contain the D-line to be suppressed in greater measure. The small amount of the second doublet component in the primary excitation of the sodium atoms was determined by special measurements and later taken into account in the calculation of the impact numbers.

The entire D-line monochromator was built into a thermostatic chamber, so that the temperature remained constant at approximately $\pm 0.02^\circ\text{K}$ and made it possible to adjust the quartz plate, as indicated by supplementary tests at certain time intervals.

33. Resonance Vessel, Furnace and Temperature Measurement

Since the resonance vessel was obliged to withstand the effect of sodium vapor at high temperatures for a long period of time (approximately 100 hours), it was necessary to make the cuvette of sodium-resistant glass and to avoid using optically perfect flats for the irradiation and observation. The sodium-resistant two-layered glass was in the form of tubes with an outside diameter of approximately 14.5 mm; it has been found to be more difficult to work than ordinary types of glass. Experiments have shown that it was most advantageous to blow a "right-angle corner" with the tube and otherwise leave it unchanged. Thus, the cuvettes were given the shape shown in Figure 2. The excitation took place through one side of the "corner" and the fluorescence was observed through the other. The light transmitted by the sodium vapor left the resonance vessel at a point at which the glass tube was left in its original form. It is true that certain reflections could be avoided on the walls by using a Wood horn, but the transmissivity measurements would no longer have been possible. In an additional tube, the sodium metal was distilled when the cuvette was charged. This metal had been previously subjected to numerous carefully performed purification processes [14]; even slight impurities could lead to significant errors in the experimental results, as shown by the experiments of Wood and Mohler [2] /61 and the measurements of Lochte-Holtgreven [3].

The internal tube of the horizontally mounted furnace, about 35 cm long, contained a twin-filament heating coil. In the middle, there was a diaphragm that was used to hold the cuvette. The rectangular opening of the diaphragm (width: 2 mm; height: 5 mm) could be adjusted horizontally, so that the distance of the exciting beam from the wall of the resonance vessel through which it was being observed could be changed. The internal tube contained a quartz window (8 mm in diameter) used for studying the fluorescent light perpendicular to the exciting beam. The temperature of the sodium vapor was monitored constantly during the

experiment with the aid of thermal elements embedded in depressions provided in the resonance vessel; with small temperature changes, the heat flux intensity could be regulated. Thus, the temperature was maintained constant during the spectral recordings lasting usually about one hour on the average. The maximum deviations that occurred during this time were always less than 1°K even at the highest experimental temperatures.

34. Experiments

A total of twenty experimental series using pure sodium vapor were performed, as well as on a sodium-potassium vapor mixture and a sodium vapor-air mixture, lasting 36 hours or more each. The course of each experimental series was such that the temperature inside the resonance vessel was increased stepwise and then reduced again, with fluorescent studies with the spectrograph and PSEV being performed simultaneously with transmissivity measurements. The two PSEV's were tested repeatedly for changes in their sensitivity and the intensity of the light emitted by the sodium spectral lamp was constantly monitored. The totality of all the measurements ensured the reproducibility of experimental results.

Hence, all spectral recordings of an experimental series could be recorded with one plate, and the latter was shifted by 1.5 mm in the cassette. Correspondingly, all recordings of the D-lines could be recorded in a series; thus, the photometry was considerably facilitated. This was accomplished by means of a Zeiss high-speed photometer; the density at several points in the spectral lines could be determined, and the various distances y of the "observation lines" could be related to the front of the cuvette. The density curves required for evaluation were obtained on the basis of calibration recordings. These were made before or after each individual experiment series with the aid of a second sodium spectral lamp; there was also an interference filter, transparent only to the D-lines, a gray filter, which reduced the intensity to the maximum observed intensity of fluorescent radiation, and an interchangeable gray filter through which the light flux could be attenuated stepwise to a known degree in the beam path.

For a complete description of the experimental conditions, it is necessary to describe the shape of the exciting D-line. This can be determined from the dependence of the transmissivity of the sodium vapor in the resonance vessel on its temperature. The shape and width of the absorption line is determined exactly by the temperature of the saturated sodium vapor and can be calculated by means of a method described previously [15]. The sodium vapor pressure of the spectral lamp in the operating state is approximately 10^{-5} at [16] and therefore corresponds to a temperature of approximately 550°K. The Doppler width of the hyperfine structural components of the D-lines emitted by the light source was therefore in the temperature range in which the significant fluorescence measurements could be carried out, and was only slightly larger than or equal to hyperfine structural components of the absorption lines. The eigenpressure width is approximately the same as that of the natural line width Δv_N in the corresponding vapor densities according to K. Watanabe [17] and H. M. Foley [18]. Since the spectral lamps have a neutral gas charge of argon between 10 and 20 Torr to initiate the metal vapor discharge, according to W. Schuetz [19] the impact width due to the addition of the foreign gas must be between 13 and 26 Δv_N . The intensity ratio of the D-lines emitted by the spectral lamp should therefore be 2:1 according to the statistical weights of the two 3^2P states. However, the measurements give 1.2:1. The explanation for this lies in the appearance of numerous reabsorptions and reemissions of the resonance radiation within the sodium vapor, in which there is a certain temperature drop toward the outer walls. This also leads to a reversal of the lines. It is quite evident that this really was the case from the transmissivity measurements which were carried out simultaneously with fluorescence measurements in the manner described in section 34. The transmissivity D for the D-lines at a vapor density $N = 1.045$ atoms/cm³ was about a power of ten larger than would be expected in this case if the incident line and the absorption line were identical in shape and width. Over a relatively broad range, the curves for the transmissivity as a function of vapor density have a shape which is described by the relationship $D = \beta(\pi k_p \rho)^{-1/2}$; here, k_p is the absorption coefficient

calculated for the absorption line [15] at the middle of the line and ρ is the density of the gas layer. The equation is valid at high optical densities if the line to be absorbed and the absorption line are both expanded by damping and the ratio of the halfwidths is equal to β . β has a value of approximately fifteen from the measurement curves, as would be expected due to the pressure distribution due to the fact that the spectral lamp is filled with a background gas.

4. MEASUREMENTS OF THE FLUORESCENT LIGHT FLUX WITH PSEV

A PSEV was used to determine the fluorescent light flux I which came from a volume that bounded the front wall of the cuvette and struck at a certain solid angle. From the results we can gain some idea about the processes in the sodium vapor. In Figures 4a and 4b, the intensity of the fluorescent light in the case of irradiation of the D_1 or D_2 -lines is plotted as a function of temperature. All measurement curves show a maximum. If the D_2 -line is used for irradiation, the latter occurs at a lower temperature than is the case when a D_1 -line is employed for primary excitation. Furthermore, the position of the maximum is determined by the distance x_m of the average plane of the incident beam on the wall of the resonance vessel, through which it is observed. With decreasing x_m , the maximum shifts toward higher temperatures and the maximum intensity of the measured fluorescent light becomes greater.

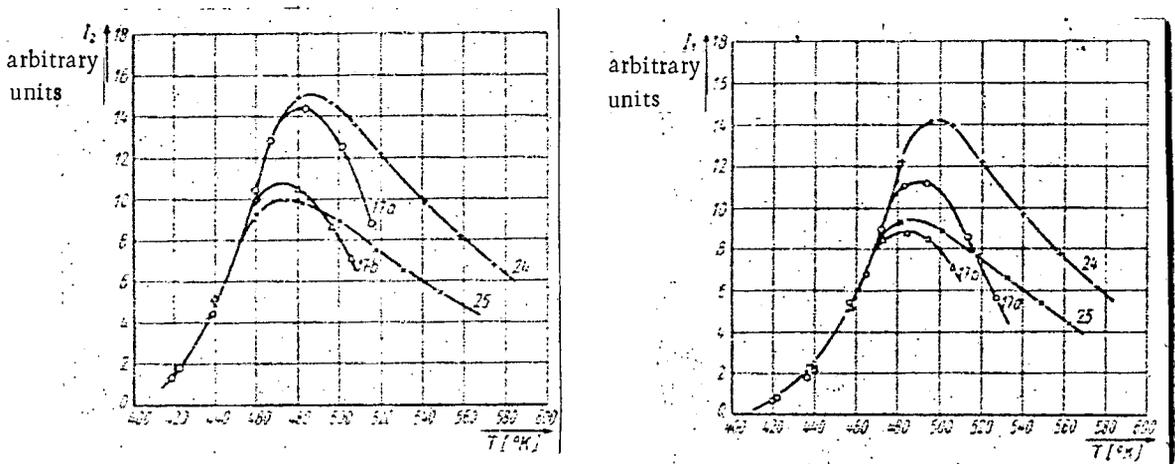


Figure 4. Intensity of the Fluorescent Light As a Function of the Temperature of the Sodium Vapor in the Case of Irradiation of the D_1 -Line (a) and the D_2 -Line (b). Experimental series No. 24 ($x_m = 2.5$ mm) and No. 25 ($x_m = 5$ mm); Pure sodium vapor; Experimental series No. 17a ($x_m = 3$ mm) and No. 17b ($x_m = 5$ mm); sodium vapor-air mixture.

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The increase in the fluorescent light flux with increasing temperature T can be understood as follows: with an increase in T , the vapor density in the cuvette rises; this also leads to an increase in absorption and the density of the excited sodium atoms increases as well. This means that the intensity of the fluorescent radiation becomes greater. The relatively steep rise will last until most of the incident light is absorbed in volume which can be absorbed through the window in the inner tube of the furnace. This means that I can increase only to an ever decreasing degree, until no significant rise in the number of excited atoms in the volume in question is possible any longer. As a matter of fact, however, the dependence of the fluorescent light flux upon temperature is different. As has already been shown by R. W. Wood [20], the "beam fluorescence" gradually becomes a "volume fluorescence." The reason for this is that the fluorescent light is reabsorbed with increasing vapor density to an ever increasing degree within the resonance vessel, and the resonant radiation propagates in the sodium vapor. However, this means that the light flux I decreases within the specified solid angle to a considerable degree. A maximum for I must appear at a certain vapor temperature. Moreover, because steadily increasing vapor density means very high values for the density of the excited atoms in the immediate vicinity of the front surface (gradual) transition from "volume fluorescence" to surface fluorescence", the probability for radiation through the surface in favor of emission through the side walls increases. Since the absorption coefficient is greater for NaD_2 than for NaD_1 , the rise in the fluorescent light flux with temperature in the case of irradiation with the D_2 -line is steeper than with the primary excitation used in the D_1 -line and radiation diffusion occurs even at low vapor densities, so that the above-mentioned maximum of I is found at lower temperatures.

The smaller the distance x_m between the middle level of the excited beam and the side wall through which observation takes place, the smaller the influence of the radiation diffusion on the fluorescent light passing through this surface; its maximum intensity is correspondingly greater by an equal degree and the maximum is found at higher temperatures.

When foreign gases are added, the second resonance line is found at lower temperatures than in a pure sodium vapor; this means that the pattern of the curves $I = I(T)$ is influenced. In experimental series No. 17b (sodium vapor-air mixture), the transitions between the two 3^2P states is a result of collisions took place to a marked extent at approximately $460^\circ K$. In the case of primary excitation with D_2 , the D_1 -line was maintained in fluorescent light. In this case, however, the effect of the radiation diffusion was less and correspondingly a greater fluorescent light flux was obtained at the same temperatures than was the case for pure Na vapor. The reverse is true with irradiation using D_1 -lines.

The foreign gases which are added may have an extinguishing effect upon the fluorescence and this will mean that the curves $I = I(T)$ will drop off more steeply than is the case for pure Na vapor. This was also shown by the measurements for experimental series No. 17a and 17b.

5. n-Measurements Using Pure Sodium Vapor

Figures 5a and 5b show the results of two experimental series using pure sodium vapor; other measurement series agree with them. In series No. 21, the distance x_m of the middle level of the incident beam from the glass wall through which the fluorescent radiation was observed was only 2 mm (and only 5 mm in series No. 25). For the individual measurement temperatures, the intensity ratio for various distances y of the "observation lines" from the front wall are given. It remains to be determined what volume elements contribute to fluorescent radiation at a certain y . If the middle level of the exciting light beam is imaged sharply on the spectrograph slit, as shown in Figure 6, point P on this plane will correspond to a very specific point P' of the slit and the latter in turn to a very particular point on the spectral line on the photographic plate. However, not only fluorescent radiation from the volume element at P passes through the surface element at P', but from a double cone, whose point is at P and whose aperture angle is given by the diameter of the imaging lens and its distance from P. The midline of the double cone has heretofore always been designated as "observation line."

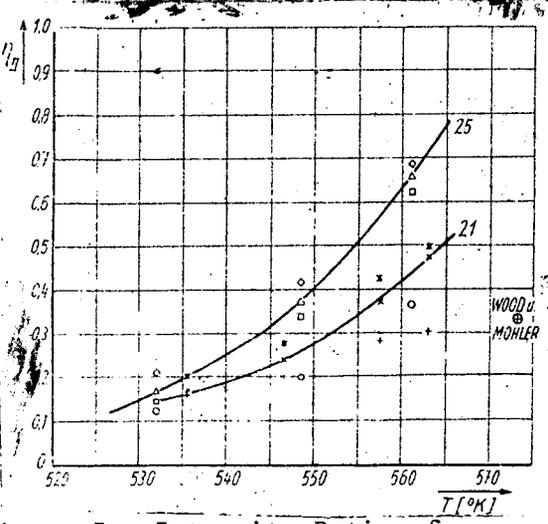
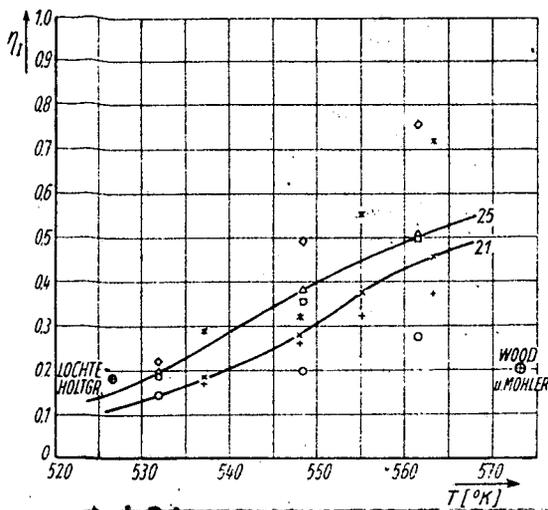


Figure 5. Intensity Ratio of D-Lines in Fluorescent Light During Irradiation of D₂-Line (a) and D₁-Line (b) in Pure Sodium Vapor. Experimental series No. 21: $x_m = 2$ mm, $y = 1.0$ mm (+), 2.3 mm (×) and 3.4 mm (*); Experimental series No. 25. $x_m = 5$ mm, $y = 0.5$ mm (○), 1.7 mm (◻); 2.5 mm (Δ) and 3.9 mm (⊙).

able displacement of the "observation lines" in the vertical directions and no remarkable change in the intensity ratios.

Without exact information on the conditions under which the intensity ratios were measured, it is not possible to compare the measured values, even at a

The fact that higher values are measured for the intensity ratio at a given and therefore with a certain vapor density with an increasing distance y in the "observation lines" from the front wall, can be explained by the appearance of radiation diffusion. It has already been used to explain the results of the fluorescence measurements with the PSEV. The further the volume elements from which the fluorescent radiation comes are located from the front wall, the greater is the amount of their reabsorptions and reemissions and therefore the longer the "maintenance time" of the irradiated light quanta at which the sodium atoms and the probability for impacts with transitions between the 3^2P states occur. A corresponding influence on the measured values for the intensity ratios of the D-lines is also exercised by the distance x_m of the central plane of the incident beam from the wall through which the observation takes place, as is quite evident from Figures 5a and 5b. Since the height h of the exciting beam in these experiments was much higher or even at least equal to x_m , there was not too great a

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certain sodium vapor density, since the influence of radiation diffusion on the experimental results with different geometrical relationships is very different. If this is taken into account, the apparent contradiction between the measurements of Wood and Mohler [2] cited in Section 1 and those of Lochte-Holtgreven [3] can be explained easily.

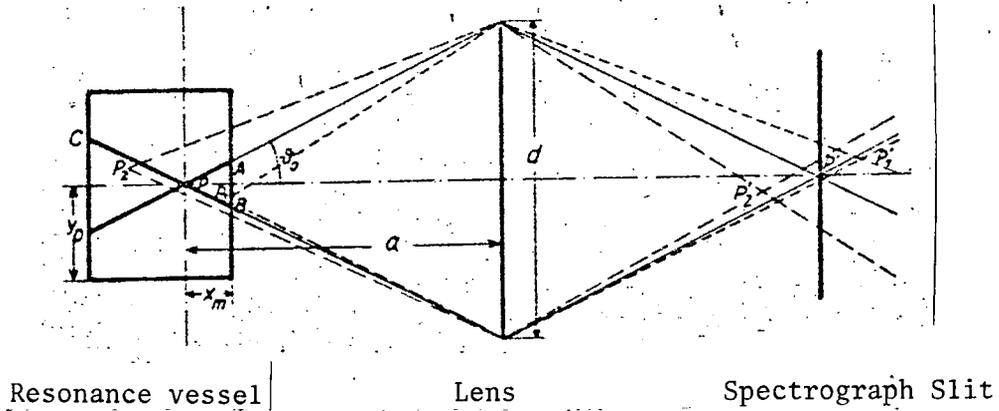


Figure 6. Imaging of the Fluorescent Sodium Vapor on the Spectrograph Slit.

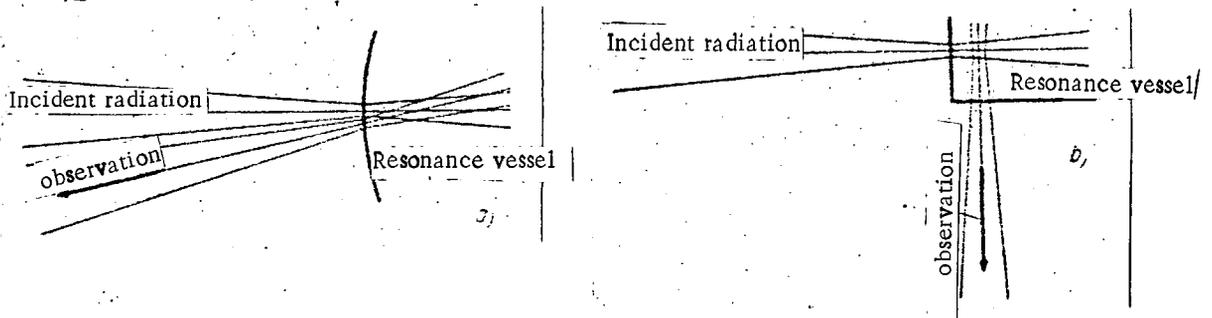


Figure 7. Diagram of Experimental Arrangements Used by Wood and Mohler (a) and Lochte-Holtgreven (b).

Lochte-Holtgreven observed the fluorescence at right angles to the exciting beam (see Figure 7), as was the case in our own experiments. This meant that a vapor layer of several millimeters lay between the beam and the wall of the resonance vessel; moreover, a diaphragm was used for the fluorescent light. Accordingly, the measurement results of experimental series No. 25 ($y = 2.5-3.9$ mm) must agree with the values given by Lochte-Holtgreven; this is the case as we

can see from Figure 5a. Wood and Mohler, on the other hand, carried out their observations at a sharp angle to the direction of incidence of the exciting beam. Therefore, the majority of the investigator fluorescent light was very close to a region where the incident light struck the sodium vapor. This resonant radiation, however, underwent much less reabsorption and reemission on its way out of the resonant vessel than was the case in the system used by Lochte-Holtgreven; hence, its dwell time in the sodium vapor was much less and therefore the chance for transitions between resonance levels due to collisions was much lower. From this it clearly follows that the same intensity ratio which was observed by Lochte-Holtgreven at 526.7°K was found by Wood and Mohler only at much higher temperatures. Our own measurements have given values that are similar to those of Wood and Mohler for $y = 0.5$ mm, in other words, observation near the front wall of the cuvette.

If we now compare the plotted curves $\eta_I(T) = I_{D1}/I_{D2}$ (radiation: NaD_2 ; see Figure 5a) and $\eta_{II}(T) = I_{D2}/I_{D1}$ (radiation: NaD_1 ; see Figure 5b), we will see that their paths initially match approximately but then $\eta_{II}(T)$ increases to a greater extent in the temperature range covered by the measurements while $\eta_I(T)$ seems to tend toward a limiting value between 0.5 and 1. The fact that this is really the case can not be seen clearly from Figure 5a, but has shown up quite obviously in other measurements. If there is no reabsorption of the fluorescent light in sodium vapor, the statistical rates of the 3^2p states accordingly at higher temperatures should reach the intensity ratio η_I with a boundary value 0.5 and η_{II} , a boundary value of 2. When radiation diffusion occurs, however, η_I can be expected to have a higher boundary value (and η_{II} a lower one).

In two previous works [15, 21], the author describes two methods in which the number of impacts on the basis of the measured intensity ratio with consideration of radiation diffusion can be calculated. A brief discussion should be inserted here. If the fluorescent radiation can leave the resonance vessel without reabsorption, the following "balance equations" are valid in the present stationary case for densities of alkali atoms in the two resonant states, with these equations then being able to be used for a simple calculation of the intensity ratio of the two doublet components:

$$-\frac{1}{\tau_1} n_1 - Z_1 n_1 + Z_2 n_2 + s_1 = 0 \quad (5.1a) \quad /68$$

$$-\frac{1}{\tau_2} n_2 - Z_2 n_2 + Z_1 n_1 = 0. \quad (5.1b)$$

In the above,

n_1 is the density of the atoms in state 1, in which the atoms are affected by the radiation from one resonance line (1),

n_2 is the density of the atoms in state 2, in which the atoms result from collisions from state 1,

Z_1 and Z_2 are the impact numbers for transitions from state 1 to state 2 and vice versa,

s_1 is the number of atoms/cm³ which transfer to state 1 through irradiation of the ground state,

τ_1 and τ_2 are the average lifetimes of the excited states 1 and 2.

If the resonant radiation propagates within the vapor, the densities of the excited atoms must be written as functions of the coordinates and both equations must be supplemented by a term through which the reabsorption of the fluorescent radiation is expressed. The result is a system of two coupled integral equations for the density distributions $n_1(x, y, z)$ and $n_2(x, y, z)$. From this it is possible to calculate the intensity ratios of the doublet components in fluorescent light. If the latter aren't measured, various pairs of values will be obtained for impact numbers Z_1 and Z_2 and the calculated values can be compared for the intensity ratios with measurement results. Since a very high expenditure of time is required to determine the impact numbers on the basis of experimental results in this fashion, the other method should be used in evaluation of the results. This involves proceeding directly from the "balance equations" (5.1a) and (5.1b), and τ_1 and τ_2 are not the average lifetimes but "apparent lifetimes" of the excited states. These correspond to the "average holding times" of an irradiated light quantum of resonant frequency ν_1 or ν_2 within the vapor and hence the "effective decay time" which is obtained as a result of radiation diffusion for the two doublet components.

T. Holstein [22], for a cylinder extending from $-\infty$ to $+\infty$ in height and with radius R , has obtained equations for calculating the "effective decay time" for various kinds of line propagation. It remains to be determined how this can be used to determine the "apparent lifetimes." Due to the pronounced decrease in the intensity of the fluorescent light with an increase in the distance y of the "observation lines" from the front wall, η -measurements are possible only for a small y -interval. The intensity ratios of the D-lines which are observed are affected only very slightly by the density distribution in the regions which are located further from the front wall, since in the latter, the densities of the atoms in states 1 and 2 are very small and correspondingly their reciprocal effect on the particles that are located closer to the front wall of the resonance vessel through the medium of radiation diffusion is small. They are also only slightly dependent upon the density distributions in the areas of the resonance vessel which (as seen by the observer) are located further away from the exciting beam, due to the pronounced absorption and the low density of the excited atoms. Then in a certain approximation one can use a basic area with width $2x_m$ and length x_m for the calculations. Moreover, in these experiments the halfheight of the exciting beam $h/2 \geq x_m$, so that we can perform the calculation as if the resonance vessel and the incident light beam extended in height from $-\infty$ to $+\infty$, in order to obtain approximately the density distribution and the intensity ratios in the horizontal median level of the exciting beam. If we go one step further and replace the rectangular ground surface by a circular one with radius $R = x_m$, we can use the equations of Holstein. We can then expect that the calculated intensity ratio for intervals y will be valid for the "observation lines" in front of the front wall, which are approximately equal to $x_m/2$. As a matter of fact, the intensity ratios obtained in this fashion do not vary very much from those which are given by the exact method in which the system is solved by two coupled integral equations [15].

According to equations

$$Z_{12} = \frac{1}{T_{D1}} \frac{(1 + \eta_1)}{\left(\frac{1}{\eta_{11}} - \eta_1\right)} \quad (5.2a)$$

and

$$Z_{21} = \frac{1}{\tau_{D2}} \frac{(1 + \eta_{II})}{\left(\frac{1}{\eta_I} - \eta_{II}\right)}, \quad (5.2b)$$

which follow from equations (5.1a) and (5.1b), the impact numbers can be calculated directly from the measurement results from the intensity ratios.

Table 1 summarizes the impact cross-sections which were obtained on the basis of measured values for the intensity ratios of the D-lines with the aid of equations (5.2a) and (5.2b), as well as (2.7) for various temperatures⁴.

TABLE 1

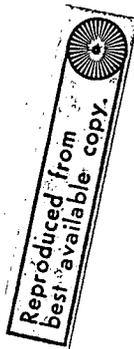
T, °K	Experimental Series No.	η_I	η_{II}	τ_{D1} sec.	τ_{D2} sec.	Q_{12} cm ²	Q_{21} cm ²
540	21 2	0.15	0.14	$1.53 \cdot 10^{-6}$	$2.69 \cdot 10^{-6}$	$1.57 \cdot 10^{-14}$	$1.01 \cdot 10^{-14}$
	25 5	0.24	0.21	$3.50 \cdot 10^{-6}$	$5.29 \cdot 10^{-6}$	$1.22 \cdot 10^{-14}$	$0.90 \cdot 10^{-14}$
	average values:					$1.40 \cdot 10^{-14}$	$0.96 \cdot 10^{-14}$
550	21 2	0.27	0.22	$2.34 \cdot 10^{-6}$	$3.61 \cdot 10^{-6}$	$1.29 \cdot 10^{-14}$	$0.99 \cdot 10^{-14}$
	25 5	0.35	0.35	$1.66 \cdot 10^{-6}$	$6.23 \cdot 10^{-6}$	$1.34 \cdot 10^{-14}$	$0.88 \cdot 10^{-14}$
	average values:					$1.32 \cdot 10^{-14}$	$0.94 \cdot 10^{-14}$
590	21 2	0.38	0.37	$3.21 \cdot 10^{-6}$	$4.84 \cdot 10^{-6}$	$1.27 \cdot 10^{-14}$	$0.86 \cdot 10^{-14}$
	25 5	0.45	0.58	$5.36 \cdot 10^{-6}$	$8.33 \cdot 10^{-6}$	$1.46 \cdot 10^{-14}$	$0.75 \cdot 10^{-14}$
	average values:					$1.37 \cdot 10^{-14}$	$0.82 \cdot 10^{-14}$

Note: Commas equal decimal points.

If we compare these results with the maximum cross-section estimated in section 2, we will see that the maximum of the characteristic curves for the velocity dependence of the cross-sections has by no means been reached. This is in agreement with the fact that for the expression $\Delta E a / h v_r$ we obtain approximately the value 3 and correspondingly the probability for the appearance of transitions in the approach of the atoms to a distance $r \leq a/2$ is still relatively small.

According to the theory of E. C. G. Stueckelberg [3], we can estimate that with an increase in the kinetic energy of the impact partners by ΔE , the energy

⁴ The η_I and η_{II} values given in Table 1 have already been corrected according to the measurements in which the relative intensity of the second D-line in the exciting light was determined (see section 32), τ_{D1} and τ_{D2} are average values calculated using approximations $D \sim \rho^{-1}$ and $D \sim \rho^{-1/2}$, "apparent lifetimes" of the excited states $3^2P_{1/2}$ and $3^2P_{2/3}^{15}$.



differential between the two 3^2P terms, the impact cross-section q_{12} and q_{21} should increase by about 10%. The values calculated in Table 1 do not indicate such an increase in cross-sections Q_{12} and Q_{21} . The average values for the two measurement series at a given temperature remain within the investigated short temperature interval which can be obtained only from the measurements and which remain essentially constant. Thought should be given to the fact that the accuracy of the method is not sufficiently great for evaluation of the measurement series in order to be able reliably to determine such a change in the cross-sections with temperature, especially because the necessary values for the transmissivity at $T = 540$ and $550^\circ K$ must be calculated from those obtained for $T = 560^\circ K$ [15]. /70

At $560^\circ K$ the average kinetic energy of relative motion is 34 times as great as energy difference ΔE between the two 3^2P terms. If an increase of 10% in the cross-sections within a temperature range of $16.5^\circ K$, which corresponds to the change ΔE of the average kinetic energy of the relative movement of the impact partners, is used as the basis, $\epsilon = Q_{12}/Q_{21}$ will be approximately equal to 1.75. This value is almost reached for $T = 560^\circ K$, as we can see from Table 1; on the average, however, it is 1.5 in the temperature interval in question. This deviation, however, may be due to the fact that in the conversion of the transmissivity for temperatures $T = 540$ and $550^\circ K$ there was no avoidance of a certain degree of inaccuracy of the values, as we have already mentioned.

In the case where fluorescent extinction took place in the investigative temperature range, this would have to have been taken into account in evaluating the measurement results. Thus far, however, there are no experimental results which indicate the appearance of extinction processes in higher sodium vapor densities. They would have made themselves evident in the form of a decrease in the calculated value for the impact cross-section with increasing temperature and at values of Q_{12} would make themselves more evident than in those with Q_{21} . This does not show up in the values summarized in Table 1, however.

The following must be taken into account before giving the final results: In the intensities of the D-lines measured for a given y -value, as was already mentioned at the beginning of this section, the fluorescent light came from a double cone. This meant that the radiation from the layers near the wall through which observation took place had the highest intensity. Because the intensity ratio of the D-lines in the fluorescent radiation decreases (but its intensity increases) the closer the part of the double cone from which they came is located to the front wall of the cuvette, lower η -values were measured for a certain y than was the case for a very small aperture angle $\Delta\omega$. In one previous paper [15], the intensity ratios η_I and η_{II} are calculated for the same conditions and impact numbers in different ways, once according to the approximation method with equations (5.1a) and (5.1b) used as a basis and another time in which the integral equation system was initially solved to give the density distributions of the excited atoms and then the relative intensities of the two resonance lines were determined assuming that $\Delta\omega > 0$. According to the approximation method, η_I and η_{II} obtained values that are somewhat too low in comparison to those obtained by more exact methods. On the other hand, on the basis of the measurement results for the intensity ratios which were less than in the case $\Delta\omega > 0$ according to previous articles, the impact numbers were calculated with the aid of the approximation method [equations (5.2a) and (5.2b)], a definite compensation must have taken place in the values calculated for Q_{12} and Q_{21} should at most be slightly less than the actual values. /71

It must be taken into account, however, that in the theoretical discussion of radiation diffusion it is assumed that of the atoms within a volume element, regardless of what spectral distribution the radiation absorbed from the resonant line possessed, the entire line is always emitted. This preconception was fulfilled only partially under the given experimental conditions, since the vapor density in these measurements is relatively low and correspondingly there was a highly dominant Doppler distribution. According to data of T. Holstein [22], it can be estimated that the calculation for the impact numbers and impact cross-sections has values that are approximately 20% too small.

Finally, if corresponding corrections are made in the values that have been calculated for the impact cross-sections with $T = 560^\circ\text{K}$, the final result will be: $Q_{12} = 1.7 \cdot 10^{-14} \text{ cm}^2$ and $Q_{21} = 1.0 \cdot 10^{-14} \text{ cm}^2$.

In evaluating the accuracy of the results, we must first discuss the experimental arrangement. The manufacture of the cuvettes which must necessarily involve sodium resistant two-layered glass means that the optical conditions are not as ideal as could be desired⁵. Thus, we must take into account a certain lack of accuracy in the determination of the values x_m and y ⁶. Furthermore, the accuracy of the results will be increased by reducing the beam cone of the fluorescent light used for measurement. However, due to the low fluorescent intensity, this is not possible. However, it is mainly the numerous sources of error in the evaluation of the measurement results with consideration of radiation diffusion that make it necessary to give the maximum limits of error of the final results at approximately $\pm 30\%$.

6. η -MEASUREMENTS ON SODIUM VAPOR-FOREIGN GAS MIXTURES

W. Lochte-Holtgreven [3] has studied the influence of the various foreign gases on the intensity ratio of the D-lines, as a function of the pressure of the gases involved. He selected the temperature of the sodium vapor in such a fashion that the resonance line which is not used for irradiation without the admixture of a foreign gas does not appear in the fluorescent light and is kept constant during the measurement series ($T = 443.2^\circ\text{K}$). Later, A. C. G. Mitchell and M. W. Zemansky [26], on the basis of curves for argon additives, obtain the following "very rough" values, as they themselves call them, for the cross-sections of the impact between sodium and argon atoms, in which transitions took place between the sodium resonance levels: $Q_{12} = 0.57 \cdot 10^{-14} \text{ cm}^2$ and $Q_{21} = 1.26 \cdot 10^{-14} \text{ cm}^2$ [27].

/72

⁵Considerable improvement could possibly have been achieved by use of flat disks of magnesium oxide, but such were not available [Strong, J. and R. T. Brice, *J. Ast. Soc. Amer.*, Vol. 25, p. 207, 1935.

⁶In the case of experimental series No. 21, with $x_m = 2 \text{ mm}$, in which the relative error of x_m and y was understandably larger than in No. 25, where $x_m = 5 \text{ mm}$, the intensity ratios were determined for 3 different y values, and that found for the mean value was employed to calculate the impact numbers, but in the case of No. 25 the n_I and n_{II} values for $y = 2.5 \text{ mm}$ were used.

The value $1/2$ can be expected for the ratio ϵ of the impact cross-sections according to the considerations in section 2, since at $T = 443.2^\circ\text{K}$ the average kinetic energy of the relative movement of the impact partners is already 27 times as great as the energy differential between the two 3^2P terms. In clearing up this contradiction, we must pay attention to the fact that it is precisely in the area of the curves of Lochte-Holtgreven which are important for the calculation and which have only one or even no measurement point and the curves therefore are plotted with a degree of arbitrariness which cannot be avoided. To be sure, Lochte-Holtgreven in the case of irradiation of the D_2 -line, by applying narrow diaphragms kept the distance of the exciting beam from the glass wall as small as possible and thereby try to cut down the reabsorption of the fluorescent radiation, but this seems to have succeeded only to a limited degree. Hence, the two measurement points for the lowest argon pressures scarcely indicate that the initial curve path in both cases, in which the vapor layer between the beam and the glass wall was given as "several millimeters" or "as small as possible," is quite different. For this reason, the disregard of reabsorption by Mitchell and Zemansky was not justified. If the cited curves are again used as a basis, despite the above considerations, to determine their intensity ratios for 2 Torr taking into account the reabsorption through an interposed sodium vapor with thickness ξ , the impact cross-sections summarized in Table 2 will be obtained.

TABLE 2

Thickness ξ of Na Vapor Layer	4 mm	2 mm	0 mm
$Q_{12} [\text{cm}^2]$	$1,1 \cdot 10^{-14}$	$0,9_0 \cdot 10^{-14}$	$0,7_3 \cdot 10^{-14}$
$Q_{21} [\text{cm}^2]$	$0,6 \cdot 10^{-14}$	$0,8_1 \cdot 10^{-14}$	$1,0_1 \cdot 10^{-14}$

For $\xi = 0$ (disregarding absorption) there is no complete agreement of the values in the table with those of Mitchell and Zemansky. Evidently the two authors have taken the intensity ratios for another argon pressure from the curves in their calculation of the impact cross section. Hence, the data of Lochte-Holtgreven merely suffice for estimating the approximate size of the cross-sections. Pursuant to the remarks on the experimental conditions it is appropriate to keep the value pair for $\xi = 4$ mm as the most suitable. Then we

obtain a value for the ratio ξ of the impact cross-sections which is approximately what we would expect from the discussion in Section 2. It must also be taken into account that a portion of the investigated light flux originates in a secondary and even a possible tertiary fluorescence; hence, the values listed in the table will appear to be a little too high. Accordingly, the result of the estimate will be: $Q_{12} = 1.0 \cdot 10^{-14} \text{ cm}^2$ and $Q_{21} = 0.6 \cdot 10^{-14} \text{ cm}^2$. /73

The pattern of the other measurement curves published by Lochte-Holtgreven for the dependence of the intensity ratio of the D-lines on the pressure of the foreign gases indicates that even when other gases are added (Ne-He, H₂, N₂), the cross-sections for impacts that result in transitions between the sodium resonance levels do not differ markedly from those obtained when argon is added.

If we now compare the calculated values of the cross sections for such collisions between the sodium atoms and between sodium and argon atoms, it will be seen that the Na-Na cross sections are larger only by approximately a factor of two than the corresponding Na-Ar cross sections⁷. This is in contradiction to the conclusions drawn by Lochte-Holtgreven from his measurement results: he felt that a collision between a sodium atom in one of the two 3²P states with a sodium atom in the ground state should lead (with an approximately two-hundred-fold greater probability) to a transition to the other resonance state, than a collision between an excited sodium atom and an argon atom. This estimate is incorrect, however, because Lochte-Holtgreven did not take into account the appearance of radiation diffusion at higher vapor densities. Its significant influence in the intensity ratios of the D-lines has already been discussed in Sections 4 and 5 on the basis of our own measurement results; it should be demonstrated once more, however, on the basis of further experiments. /74

⁷It should be noted that values for Q_{12} and Q_{21} determined for collision partners of different temperatures and mean kinetic energies of relative motion are here compared to each other. Because of the velocity dependence of the collision cross sections, ratios differing from these might be obtained at other sodium vapor temperatures.

During the melting of a cuvette a slight jump occurred at the previous melting point, leading to a slight air leak. If the oxygen-nitrogen pressure in the cuvette is not known, the measurement results for the intensity ratios as a function of temperature provides important data on the processes within the sodium vapor. Figures 8a and 8b present the results of three experimental series. The dependence of the intensity ratio of x_m and y , already discussed in Section 5, can also be found here and may be attributed in the same way to the influence of radiation diffusion. In the temperature range covered by the measurements, it would have been impossible to observe the appearance of the second doublet component without the addition of the foreign gas, as indicated by the experiments with pure sodium vapor. However, the density of the foreign gas was still so low that the non-irradiated D-line was missing in fluorescent light at low temperatures and therefore low sodium vapor pressures. It is only by raising the temperature and therefore the vapor density that the number of reabsorptions and reemissions was increased, thereby prolonging the "apparent lifetime" of the excited states so sharply that increasingly more frequent collisions with transitions between the 3^2P states occurred between the excited sodium atoms and the intensity ratio assumes steadily increasing values, although the collision numbers that increased at the same time were still relatively small. These studies supplement the above-mentioned experiments which Lochte-Holtgreven performed at constant temperature and variable foreign gas pressure. They demonstrate very clearly the necessity for an extremely careful purification of the sodium, since even very small admixtures of foreign gas at higher vapor densities lead to the appearance of the non-irradiated resonance line in fluorescent light and may then falsify the measurement results for "pure" sodium vapor.

If we calculate the impact numbers from the measurement curves according to the method employed in the previous section, Z_{21} remains approximately constant from 480 to 510°K, while Z_{12} decreases even with increasing temperature. Accordingly, the ratio $\zeta = Z_{12}Z_{21}$ also decreases with increasing temperature, from 2 to 1.3. Such a dependence of both impact numbers and their ratios on the temperature cannot be expected from the statements in Section 2. It should be taken into account, however, that at 480°K the vapor density is still not sufficiently high that even with the aid of the theory of Holstein [22] sufficiently accurate values could not be obtained for the "apparent lifetimes" of the

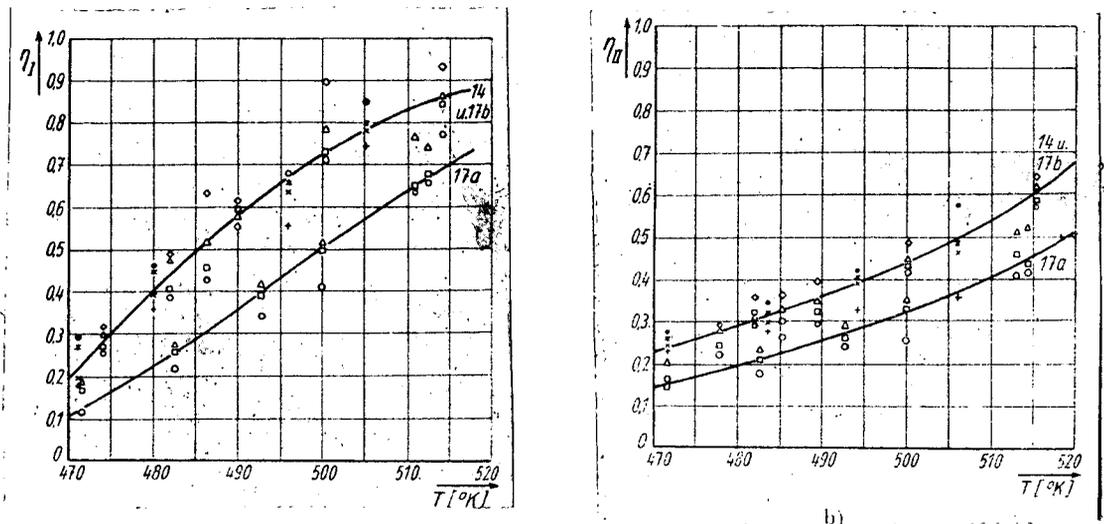


Figure 8. The Intensity Ratio of the D-Lines in Fluorescent Light During Irradiation of the D₂-Line (a) and D₁-Line (b) in a Sodium Air Vapor Mixture. Test series No. 17a: $x_m = 3$ mm, $y = 1.1$ mm (○), 1.8 mm (□) and 2.4 mm (△); Test series No. 14: $x_m = 5$ mm, $y = 1.1$ mm (○), 1.7 mm (□), 2.5 mm (△) and 3.3 mm (◇); Test series No. 17b: $x_m = 5$ mm, $y = 1.1$ mm (+), 1.7 mm (×), 2.4 mm (*) and 3.0 mm (○).

excited states. Consequently, the ratio of the impact numbers calculated for $T = 480^\circ\text{K}$ could be slightly too high. Moreover, the fluorescence extinction must be taken into account. According to R. G. W. Norrish and W. M. F. Smith [29], /75 the cross-section for extinguishing impacts between sodium and nitrogen is $5.5 \cdot 10^{-16} \text{cm}^2$; the cross section for extinguishing impacts between sodium and nitrogen should not deviate markedly. When the number of reabsorptions and reemissions is raised by the increase in the vapor density, the probability of the appearance of extinction processes and transitions between the resonance levels due to collisions increases. The "apparent lifetimes," which are critical for the frequency of these collisions, are shortened by extinction, however, and (as can be easily seen) have a stronger effect on τ_{D2} than on τ_{D1} . Since the foreign gas density is not known, a corresponding correction of the impact numbers Z_{12} and Z_{21} cannot be made; however, it may lead to an increase in the values of Z_{12} and Z_{21} , in such a way that ζ is finally between 1.8 and 2.0 in the entire temperature range.

7. n-MEASUREMENTS ON A SODIUM-POTASSIUM VAPOR MIXTURE

According to a measurement by Lochte-Holtgreven [3], the same intensity ratio of the resonance lines in fluorescent light was found (during irradiation with the D_2 -line in sodium vapor to which potassium vapor at a pressure of $p = 3 \cdot 10^{-3}$ Torr was added) as was observed for irradiation in pure sodium vapor at $p = 2 \cdot 10^{-3}$ Torr. The sodium vapor pressure was then so low that without the addition of potassium vapor the appearance of the second doublet component could not be detected. These data are insufficient, however, to allow a statement to be made regarding the impact cross-sections, since it is precisely the sodium vapor density which must be known exactly in order that the radiation diffusion may be taken into account. /76

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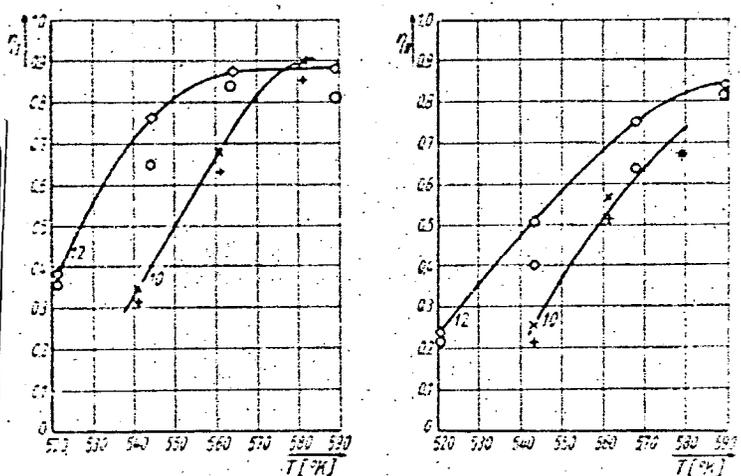


Figure 9. The Intensity Ratio of the D-Lines in Fluorescent Light During Irradiation of the D_2 -Line (a) and D_1 -Line (b) in a Sodium-Potassium Vapor Mixture. Test series No. 10: $x_m = 2$ mm, $y = 1.3$ mm (+) and 2.5 mm (x); Test series No. 12: $x_m = 5$ mm, $y = 1.4$ mm (⊙) and 3.0 mm (◊).

obtained, because the impact width of the absorption line is influenced by the potassium vapor density. In accordance with the method employed in the previous sections, the impact numbers can now be calculated. In order to obtain the

Hence, four test series were performed with a sodium-potassium vapor mixture. The measurement results of Series 10 and 12 are given by Figures 9a and 9b. At room temperature the binary system was in a fluid state. Data on the partial pressure of the two components as a function of their weight ratio and temperature are not given in the literature. The sodium vapor density can be obtained by comparing the values for the transmissivity of the pure sodium vapor and the vapor mixture. However, in the case of higher temperatures only approximately valid values can be

impact cross sections, however, it is necessary to know the potassium vapor density and the average relative velocity of the colliding partners. Since the latter changes only slightly in the narrow temperature range studied, it can be assumed to be on the average $9 \cdot 10^4 \text{ cm} \cdot \text{sec}^{-1}$. The density of the potassium atoms could be determined in the same fashion as that of the sodium atoms; however, then at higher temperatures the accuracy of the values obtained would be reduced by the influence of the sodium vapor density on the impact width of the potassium absorption line. Moreover, a significant expansion of the test apparatus would also have been necessitated; in addition, transmissivity studies using special cuvettes filled with pure potassium would have been necessary. Since it is possible to calculate the potassium partial pressure from the already available experimental results in a definite approximation, the specific potassium vapor pressure measurements can be dropped.

For the partial pressure of one component of a binary system, the following is approximately valid:

$$p = \gamma \cdot p_s; \quad (7.1)$$

where γ is the mole fraction $n/(n + n')$, i.e., the ratio of the number of moles of the two components and p_s is their saturation pressure if it occurs pure (unmixed). The given reaction corresponds to the first Raoult law; but the latter is only strictly valid for dilute solutions, however. If this condition is not fulfilled, the isothermal partial pressure curves for these different binary systems will have different shapes.

If we now apply equation (7.1) to studies of R. Minkowski [30], to a mixture of 52 wt.% sodium of 48 wt.% of potassium, we will find a very good agreement between the measured and calculated values for the mole fraction γ . It cannot be concluded from this, however, that the validity of (7.1) is ensured for all mixing ratios, but in any case it does provide usable approximate values if the mixing ratio does not differ too much from it, as was assumed in the tests of Minkowski. On the basis of the above-employed comparison of the transmissivity measurements the sodium partial pressure can be determined. The saturation pressure for the temperatures in question is known [31, 32]. It then follows that the sodium fraction is 50 mole % to 37 wt.% and so the mole fraction was 0.5 for potassium as well. The potassium saturation pressures could be calculated

using an equation given by W. Edmondson and A. Egerton [31]. The partial pressures were then determined with the aid of (7.1).

Table 3 gives the densities obtained for the sodium and potassium atoms (N_{Na} and N_K), the temperatures T_{Na} corresponding to the sodium vapor densities, the "apparent lifetimes" required for the evaluation of the measurement series according to equations (5.2a) and (5.2b) τ_{D1} and τ_{D2} , and the finally obtained impact cross sections Q_{12} and Q_{21} . If we again use the same corrections used and applied in calculating the cross sections of the collisions between sodium atoms (Section 5), we obtain the following end result: $Q_{12} = 0.6_5 \cdot 10^{-14} \text{ cm}^2$ and $Q_{21} = 0.4_5 \cdot 10^{-14} \text{ cm}^2$. In evaluating the measurement data it has not yet been taken into account that at the highest temperatures that were reached in the experimental series the number of collisions between sodium atoms in which transitions appeared between resonance levels relative to the intensity ratios measured for the sodium-potassium vapor mixture was so large that it had to be taken into account in order not to obtain overly high values for the sodium-potassium impact cross sections. On the other hand, the shape of the measured curves appears to indicate that at higher temperatures extinguishing collisions took place and that thereby the intensity ratios were decreased. $\eta_I(T)$ increases beyond 0.5 to reach a value of 0.9; this value does not quite reach η_{II} in the investigated temperature range and may not exceed it by much along the curve even with a further temperature increase. Such a low boundary value cannot be created by the influence of radiation diffusion alone, but with the simultaneous appearance of extinction processes through which the η_{II} values are more markedly depressed than the η_I values. Correspondingly, the fluorescence extinction may have had more effect on the value obtained for Q_{12} than that for Q_{21} . This could explain why the quotient $\epsilon = Q_{12}/Q_{21}$ is still much less than 2.

TABLE 3

T K	N_{Na} cm^{-3}	T_{Na} K	N_K cm^{-3}	V. R. Nr.	τ_{D1} sec	τ_{D2} sec	Q_{12} cm^2	Q_{21} cm^2
40	$2.9 \cdot 10^{13}$	521.5	$9.20 \cdot 10^{13}$	10	$0.60 \cdot 10^{-6}$	$1.14 \cdot 10^{-6}$	$4.0 \cdot 10^{-15}$	$2.3 \cdot 10^{-15}$
				12	$1.82 \cdot 10^{-6}$	$2.91 \cdot 10^{-6}$	$7.5 \cdot 10^{-15}$	$5.6 \cdot 10^{-15}$
64	$6.43 \cdot 10^{13}$	540	$1.98 \cdot 10^{15}$	10	$1.63 \cdot 10^{-6}$	$2.69 \cdot 10^{-6}$	$4.3 \cdot 10^{-15}$	$2.9 \cdot 10^{-15}$
				12	$3.50 \cdot 10^{-6}$	$5.29 \cdot 10^{-6}$	$4.2 \cdot 10^{-15}$	$3.1 \cdot 10^{-15}$
Average values							$5.9 \cdot 10^{-15}$	$3.5 \cdot 10^{-15}$

Note: Commas indicate decimal points.

Due to the error sources already mentioned in Section 5 in the measurements and especially due to the use of different approximations in the evaluation of the experimental results, one must expect a certain lack of accuracy in the final result. The limits of error (approximately $\pm 40\%$) can be reduced, however, only at much greater experimental and computer expense. The studies have already provided the important result that the cross-sections of the collisions between a sodium atom in one of the two 3^2P states and a potassium atom in which the sodium atom crosses to the other resonance state do not differ markedly from the cross-sections of similar collisions between sodium and argon atoms. This could in no way be concluded from the initially given data of Lochte-Holtgreven.

Summary

The studies in which a D-line was irradiated into pure sodium vapor, a sodium vapor air mixture and a sodium potassium vapor mixture have clearly shown that the intensity ratios of the two resonance lines in fluorescent light is markedly influenced by the radiation diffusion and that the measured values therefore depend on the geometry of the system. If this is taken into account, the apparent contradiction between the experimental results of Wood and Mohler [2] and Lochte-Holtgreven [3] can be readily explained. In calculating the cross-sections for the collisions in which transitions occurred between the two 3^2P states, the following values were obtained considering the radiation diffusion: for Na-Na collisions $Q_{12} = 1.7 \cdot 10^{-14} \text{ cm}^2$ and $Q_{21} = 1.0 \cdot 10^{-14} \text{ cm}^2$ ($T = 560^\circ\text{K}$) for Na-K collisions $Q_{12} = 0.65 \cdot 10^{-14} \text{ cm}^2$ and $Q_{21} = 0.45 \cdot 10^{-14} \text{ cm}^2$ ($T = 540\text{--}564^\circ\text{K}$). Moreover, from the measurements of Lochte-Holtgreven [3] the following cross sections can be estimated for such collisions between sodium and argon atoms: $Q_{12} = 1.0 \cdot 10^{-14} \text{ cm}^2$ and $Q_{21} = 0.6 \cdot 10^{-14} \text{ cm}^2$ ($T = 443^\circ\text{K}$). The cross sections for Na-Na collisions with transitions between the resonance levels are therefore only a factor of 2 or 3 larger than the same collisions between sodium and argon atoms or sodium and potassium atoms.

With the aid of the principle of detailed equilibrium, the dependence of the ratio of the cross sections q_{12} and q_{21} can be derived from the kinetic energy of the relative motion of the colliding partners and on the basis of "semiclassical" considerations the characteristic velocity dependence of

the impact cross-sections can be derived. The maximum cross-section to be expected for the Na-Na collisions is approximately $3 \cdot 10^{-13} \text{ cm}^2$; however, it can only appear at much higher relative velocities of the colliding partners. In the temperature range that can be merely indicated in the η -measurements, most collisions proceed adiabatically. If we assume that when the mean kinetic energy of the relative motion of the colliding partners is increased by ΔE , the energy differential between the two 3^2P terms, the cross-sections increase by 10%, so that one should expect a ratio of the impact cross-sections of $\epsilon = Q_{12} / Q_{21}$ of approximately 1.75, which is approximately what was obtained in evaluating the measurement results. /79

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